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3

One component thioxanthone based Type II photoinitiators

Nergis Arsu¹, Meral Aydin¹, Yusuf Yagci², Steffen Jockusch³
and Nicholas J. Turro³

¹Department of Chemistry, Yildiz Technical University, Davutpasa, Istanbul, 34210, Turkey

²Department of Chemistry, Istanbul Technical University, Maslak, Istanbul, 34469, Turkey

³Department of Chemistry, Columbia University, 3000 Broadway, New York, NY 10027, USA

Abstract

Thioxanthone (TX) and their derivatives are bimolecular Type II photoinitiators for free radical polymerization. Photoinitiation by these compounds is based on the reaction of their triplet excited states with a hydrogen donor thereby producing an initiating radical. On the other hand, they suffer from diffusion controlled limitation of reactivity and from deactivation by back electron transfer. In this chapter, we present a very efficient concept to raise the photoinitiator activity by covalent binding of hydrogen donating sites to the TX moiety. Mechanistic details concerning photoinitiated free radical polymerization using two classes of such one-component systems, namely thioxanthone-thiol (TX-SX) and thioxanthone

thio-acetic acid (TX-S-CH₂-COOH) are described. The contributions of intra- and inter-molecular electron transfer processes followed by hydrogen abstraction are discussed. The use of several one-component polymeric photoinitiators is also described. These photoinitiators have additional advantages of overcoming the problems in curing applications associated with low odor and toxicity, and good storage stability.

1. Introduction

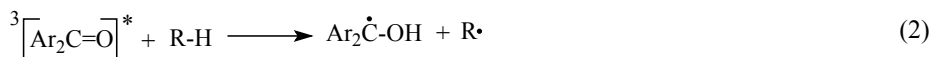
The photoinitiated free radical polymerization reactions are widely used on a commercial scale for a number of different applications such as curing of coatings on various materials, adhesives, printing inks and photorezists.¹⁻⁵

The growth of radiation curing industry is dependent on continued innovation to support this technology. A wide range of free radical photoinitiating systems, fulfilling requirements for industrial application, e.g. wavelength selectivity, solubility etc. is now available. A large portion of today's relevant research concerns photoinitiators, i.e. introduction of new initiators or improving the solubility of available initiators.¹⁻⁴ Photoinitiated radical polymerization may be initiated by both cleavage (*Type I*) and H-abstraction type (*Type II*) initiators. Because of their vital role in photopolymerization, photoinitiators are the subject of particularly extensive research. Most of this research has focused on *Type I* photoinitiators, which upon irradiation undergoes an α -cleavage process to form two radical species. *Type II* photoinitiators are a second class of photoinitiators and are based on compounds whose triplet excited states are reacted with a hydrogen donor thereby producing an initiating radical.

2. Type II photoinitiators

2.1. Aromatic ketone / co-initiator system

Photolysis of aromatic ketones, such as benzophenone, in the presence of hydrogen donors leads to the formation of a radical stemming from the carbonyl compound (ketyl type radical in the case of benzophenone) and another radical derived from the hydrogen donor (Scheme1).



Scheme 1. Photoinitiated free radical polymerization by aromatic carbonyl/co-initiator.

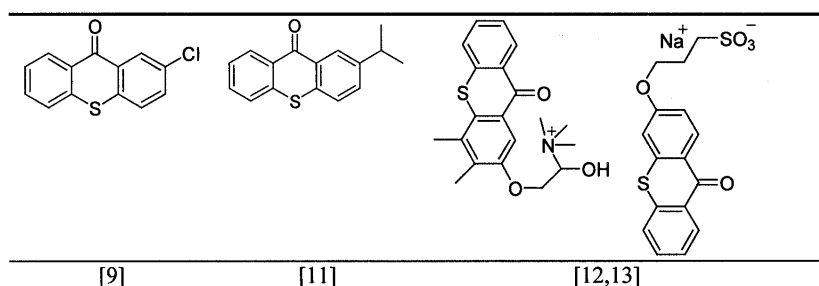
Provided vinyl monomer is present the latter may initiate a chain polymerization. The radicals stemming from the carbonyl compound are usually not reactive towards vinyl monomers due to bulkiness and/or the delocalization of the unpaired electron.

Apart from benzophenones, thioxanthone, anthraquinones, ketocoumarins and some 1,2-diketones are used in conjunction with co-initiators for initiating vinyl polymerizations. Since the initiation is based on a bimolecular reaction, *Type II*

photoinitiators initiate generally slower than *Type I* photoinitiators. These systems are, therefore, more sensitive to the quenching of the excited triplet states, which are the reactive precursors of light induced chemical changes for carbonyl compounds.

In view of applications, the selection of the co-initiator is undoubtedly of great importance. Mostly, amines are used because of their high efficiency and the relatively low price. Excited carbonyl triplet states are usually by two to three orders of magnitude more reactive towards tertiary amines than towards alcohols or ethers. Among *Type II* photoinitiators, thioxanthone derivatives in conjunction with tertiary amines are efficient photoinitiators with absorption characteristics that compare favorably with benzophenones⁶; absorption maxima are in the range between 380 to 420 nm ($\epsilon = 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$) depending on the substitution pattern. The reaction mechanism has been extensively investigated by spectroscopic and laser flash photolysis techniques.⁷⁻¹⁰ It was found that in conjunction with tertiary amines reactions similar to that of benzophenone / amine systems take place.

Table 1. Some Thioxanthone Derivatives Used as Photoinitiators.



The most widely used commercial derivatives are 2-chlorothioxanthone and 2-isopropylthioxanthone. Furthermore, ionic thioxanthone derivatives have been developed, which may be employed for water based curing formulations^{12,13} (Table 1).

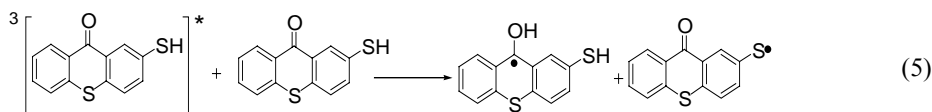
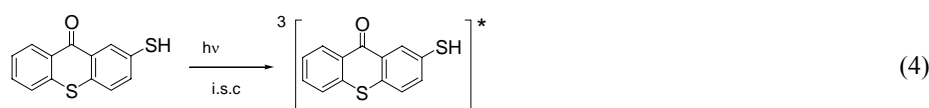
2.2. One-component *Type II* photoinitiators

Recently, we have introduced several thioxanthone derivatives as a new class of *Type II* photoinitiators for free radical polymerization of olefinic compounds. The pronounced initiating capacity of these compounds is based on the fact that both light absorbing and hydrogen donating sites are composed in one molecule. In accordance with the mode of formation of free radicals, they are called as one-component *Type II* photoinitiators. The thioxanthone structure was selected for two reasons. First, in photoinitiated free radical polymerization applications quite frequently problems arise with respect to the selection of appropriate initiators, the light absorption of which should not be screened by the additives. In this connection thioxanthone derivatives are notable because they are capable of overcoming these difficulties to a certain extent, by having absorption bands in the near UV wavelength range. Secondly, desired substituents can easily be incorporated into thioxanthone structure by a simple coupling reaction. Photopolymerization, laser flash photolysis and time resolved fluorescence studies

devoted to this class of initiators are described in this chapter. Prior to dealing with details the mode of action of one-component photoinitiators shall be pointed out.

2.2.1. 2-Mercaptothioxanthone(TX-SH)

2-Mercaptothioxanthone (TX-SH) possesses an absorption characteristic similar to the parent thioxanthone with a maximum at 383 nm ($\epsilon = 3857 \text{ L mol}^{-1} \text{ cm}^{-1}$). This high molar absorptivity makes TX-SH attractive as a photoinitiator because of its efficient light absorption. TX-SH can be used as a photoinitiator for the polymerization of vinyl monomers in the presence and absence of air.



Scheme 2. Photoinitiated free radical polymerization by TX-SH.

The mechanism depicted in Scheme 2 is based on the intermolecular reaction of triplet, ${}^3\text{TX-SH}^*$, with the thiol moiety of ground state TX-SH. When TX-SH was irradiated in the presence of a monomer, it was found that it can serve as both a triplet photosensitizer and a hydrogen donor. The resulting thiyl radicals initiate the polymerization.

Intramolecular hydrogen abstraction is not likely to occur because of the fused benzene ring on which thiol group stands. Indeed, this possibility was experimentally excluded by laser flash photolysis studies. Flash photolysis (355 nm excitation) of a highly diluted solution of TX-SH affords a readily detectable transient absorption spectrum, which decayed in a first-order kinetic with a lifetime of 20 μs (Figure 1).

Transient absorption and lifetime was similar to the triplet-triplet absorption of the parent TX.^{14, 15} Therefore, it was concluded that the transient absorption corresponds to the triplet-triplet absorption of TX-SH. If intramolecular hydrogen abstraction would dominate, than the transient decay kinetic should be significantly faster. This is consistent with an unfavorable interaction of the excited carbonyl group with the thiol moiety caused by the rigidity of the linked aromatic groups. Similar limitations were accounted for Michler's ketone^{15, 17} as a photoinitiator which also possesses both chromophoric and hydrogen donating sites. Phosphorescence spectra of TX covalently attached polymers provided further evidence for the initiation mechanism. Phosphorescence

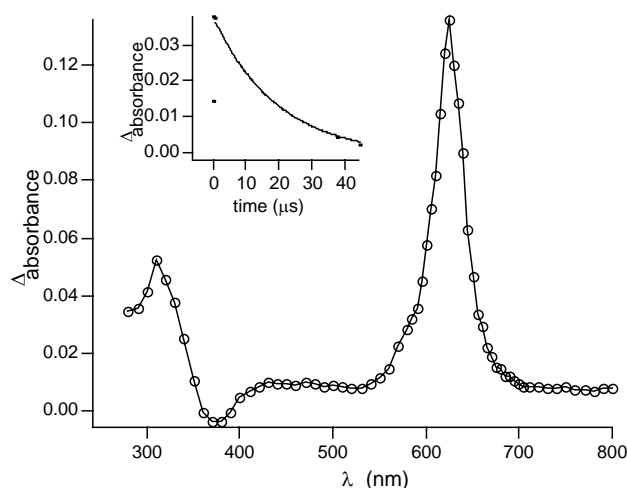


Figure 1. Transient optical absorption spectrum recorded 1-5 μs following laser excitation (355 nm, 5 ns) of 2-mercaptothioxanthone (TX-SH) (1×10^{-4} M) in argon-saturated acetonitrile solution at 23°C. Insert: Transient absorption kinetic observed at 625 nm.

spectra in 2-methyltetrahydrofuran at 77 K of TX-SH and PMMA obtained from photopolymerization initiated by TX-SH were very similar.¹⁸ It was also found that the excitation spectra for the emission signal are in good agreement with the absorption spectra of TX-SH.¹⁸ The phosphorescence lifetimes at 77 K, were also very similar; 147 ms and 145 ms, respectively. Thus, various spectroscopic investigations revealed that thioxanthone groups are incorporated into the polymers.

This odorless new photoinitiator is very attractive, since it does not require an additional hydrogen donor and initiates the polymerization of both acrylate and styrene monomers in the presence and absence of air. In addition, TX-SH possesses excellent optical absorption properties in the near UV spectral region, ensuring efficient light absorption from most UV-curing tools.¹⁸

The efficiency of the TX-SH in the photocuring of formulations containing multifunctional monomers was also studied and compared with that of the two component systems. The disappearance of double bonds during the photocuring of the formulations was followed by Fourier transform real-time spectroscopy (RTIR) that has spread out widely in recent years. By monitoring changes in the characteristics monomer IR absorption bands it allows to follow fast polymerization process continuously. In Figure 2 kinetic profiles referring to the polymerization of the mixture epoxyacrylate and tripropyleneglycoldiacrylate under polychromatic light are shown. TX-SH and TX/*N*-methyldiethanolamine (MDEA) served as photoinitiators. The curves were obtained by monitoring the absorption decrease of the band at 810 cm^{-1} corresponding to the frequency of the twisting vibration of the double bonds. The shape of the curves indicates the existence of two stages - a rapid first stage which is followed by a slow stage. It can be seen that at sufficiently high concentrations polymerization takes place more rapidly with TX-SH than that of the corresponding with TX/MDEA.

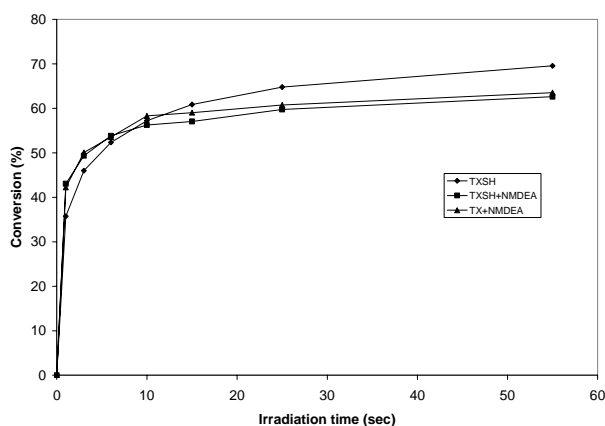
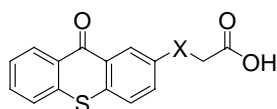


Figure 2. Kinetic profiles demonstrating the photopolymerization of trimethylol propantriacyrylate containing different photoinitiators with polychromatic light. Photoinitiator (1 %): (◆)TX-SH (■) TX-SH and NMDEA, and (▲) TX and NMDEA.

2.2.2. Thioxanthone acetic acid derivatives

Another one-component photoinitiating system developed in our laboratory is thioxanthone acetic acid derivatives of the following structure. Also in this case, the light absorbing and electron donating and, consequently, hydrogen donating sites are in the photoinitiator molecules.

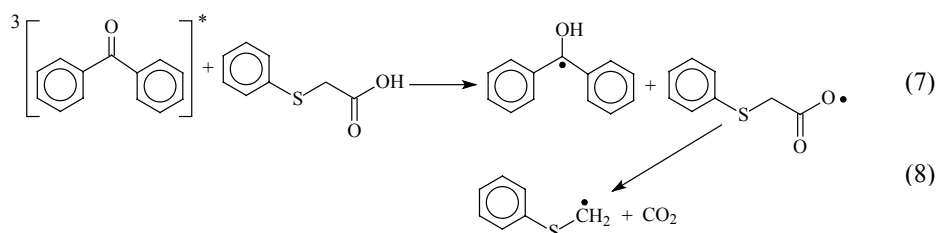


X: O,S

Chart 1. The structure of thioxanthone acetic acid derivatives.

Early mechanistic studies on two component systems of this type suggested an aromatic carbonyl sensitized decarboxylation mechanism. According to Davidson and co-workers^{19, 20}, excited aromatic carbonyl compounds such as benzophenone can undergo electron transfer with sulfur- or oxygen-containing carboxylic acids to give carboxylate radicals. Subsequent decarboxylation of this radical produces an alkyl radical as represented on the example of benzophenone/thiophenoxy acetic acid couple in Scheme 3.

As the other thioxanthone derivatives, thioxanthone thio-acetic acid (TX-S-CH₂-COOH) has an excellent optical absorption in the near UV ($\epsilon_{290} = 20490 \text{ mol}^{-1} \text{ L cm}^{-1}$ and $\epsilon_{384} = 3900 \text{ mol}^{-1} \text{ L cm}^{-1}$). In view of the decarboxylation behavior^{19, 21, 22} of the sulfur containing carboxylic acids upon reaction with photoexcited aromatic carbonyl compounds as depicted in Scheme 3), photolysis of TX-S-CH₂-COOH results in the



Scheme 3. Hydrogen abstraction and decarboxylation reactions of excited benzophenone and thiophenoxy acetic acid.

formation of free radicals. The decarboxylation nature of the photoinitiation was demonstrated by concomitant evolution of carbon dioxide. In order to clarify the mechanistic details, we performed steady state and time-resolved fluorescence and laser flash photolysis measurements together with polymerization experiments.

The quantum yield for fluorescence emission (ϕ_f) in 2-methyl tetrahydrofuran at 23 °C was found to be 0.06 which is similar to that of unsubstituted thioxanthone. Steady-state and time-resolved excitation and emission spectra of TX-S-CH₂-COOH were also measured at 77 K in the same solvent. The two emission bands were found at 430 nm and 508 nm and are attributed to fluorescence and phosphorescence, respectively. Phosphorescence measurements were useful to gain information on the triplet configuration of TX-S-CH₂-COOH. In addition, the phosphorescence lifetime for n - π^* triplets were significantly shorter (in the order of several milliseconds) compared to π - π^* triplets (more than 100 ms).^{16, 23} Thus, the broad structureless phosphorescence of TX-S-CH₂-COOH, together with the long phosphorescence lifetime, i.e. 127 ms in a matrix at 77 K, indicates a π - π^* nature of the lowest triplet state. This was in agreement with the π - π^* nature of the lowest triplet state of unsubstituted TX²⁴ and also with TX-SH.¹⁸

To investigate the triplet state of TX-S-CH₂-COOH further, laser flash photolysis was performed. Figure 3 shows the transient absorption spectra of a deoxygenated acetonitrile solution containing TX-S-CH₂-COOH recorded 10-30 ns and 300-400 ns after irradiation with laser pulses of 355 nm. The spectrum shows two peaks at 660 nm and 340 nm. The peak at 660 nm was assigned to the triplet-triplet absorption of TX-S-CH₂-COOH based on similarities with the triplet-triplet spectra of TX and TX-SH.¹⁸ Figure 4 (right) shows the decay kinetic of the transient absorption at 660 nm. The triplet-triplet absorption at 660 nm decayed in a first-order kinetic corresponding to a lifetime of 65 ns. In contrast, the transient absorption at 340 nm decayed orders of magnitudes slower (12 μ s) (Figure 4, left). Notably, both transients were quenched by oxygen with rate constants close to the diffusion limit ($k_{O_2}^{340\text{ nm}} = 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{O_2}^{660\text{ nm}} = 4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) suggesting a radical or triplet nature of the transients.

Typically, triplet states of TX derivatives, such as TX or TX-SH possess triplet lifetimes longer than 10 μ s (TX-SH: $\tau_T = 21 \mu$ s).¹⁸ In contrast, TX-S-CH₂-COOH showed a triplet lifetime of only 65 ns, which indicates the involvement of a fast intramolecular quenching process. We proposed that the fast intramolecular quenching process was a fragmentation reaction leading to carbon centered radicals (see below),

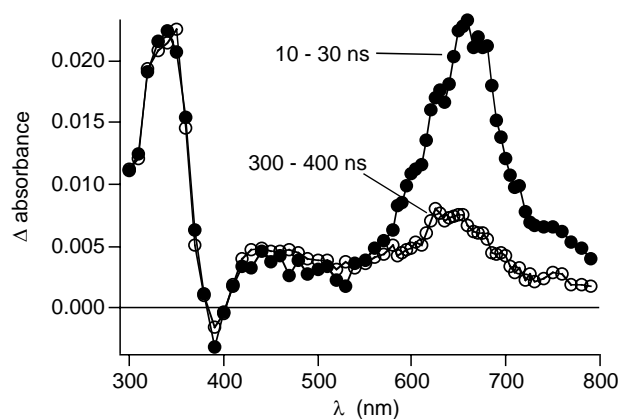


Figure 3. Transient optical absorption spectrum recorded 10 – 30 ns and 300 – 400 ns following laser excitation (355 nm, 5 ns) of TX-S-CH₂-COOH in argon saturated acetonitrile solution at 23 °C.

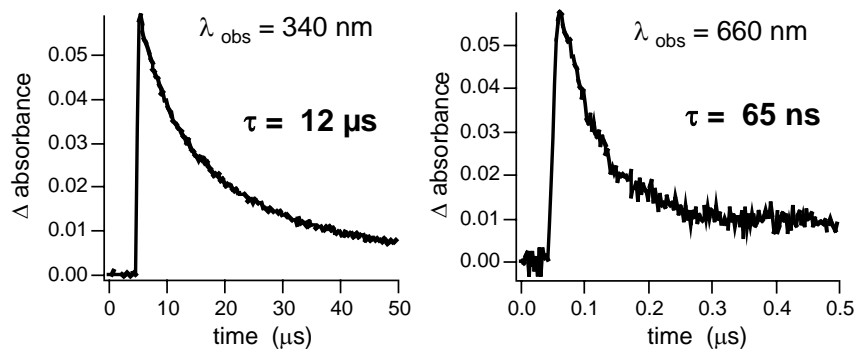


Figure 4. Transient absorption kinetics observed at 340 nm (left) and 660 nm (right) following laser excitation (355 nm, 5 ns) of TX-S-CH₂-COOH in argon saturated acetonitrile solution at 23 °C.

which than can initiate the polymerization. To test, if triplet quenching occurs in an intramolecular process or intermolecular process, laser flash photolysis experiments were performed at two different concentrations of TX-S-CH₂-COOH, 2.5×10^{-5} M and 5×10^{-5} M. At both concentrations, an identical triplet lifetime (65 ns) was observed, showing that at these low photoinitiator concentrations no intermolecular reaction occurs, where the triplet of TX-S-CH₂-COOH gets quenched by another molecule of TX-S-CH₂-COOH in the ground state. Furthermore, such a bimolecular quenching process is unlikely at these low concentrations of TX-S-CH₂-COOH (5×10^{-5} M), because of the short triplet lifetime (65 ns).

To investigate if bimolecular quenching can occur at higher concentrations, a model compound was used, thiophenoxyacetic acid (Ph-S-CH₂-COOH), as quencher of triplet

states of TX-S-CH₂-COOH (analog reaction in Scheme 3). Laser flash photolysis experiments were performed with deoxygenated acetonitrile solutions of TX-S-CH₂-COOH (5×10^{-5} M) and different concentrations of Ph-S-CH₂-COOH ($0 - 2.5 \times 10^{-2}$ M). Pseudo-first order treatment of the decay kinetics of the TX-S-CH₂-COOH triplet states observed at 660 nm gave a quenching rate constant of $8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. This shows that a bimolecular quenching process, where the triplet of TX-S-CH₂-COOH gets quenched by another molecule of TX-S-CH₂-COOH in the ground state, can only compete with the intramolecular quenching at concentrations in the order of several mM.

We also performed polymerization experiments. The dependence of conversion of methyl methacrylate to polymer upon irradiating in DMF in air, on the concentration of the initiator, is shown in Figure 5. Initially, the rate of initiation is proportional to the absorbed light and consequently the amount of initiator. However, when the concentration of the initiator was above a certain level the intermolecular hydrogen abstraction may become a dominant process. Therefore, the formation of free radicals capable of initiating polymerization, was determined by the competition of intra and intermolecular hydrogen abstraction processes. Indeed, the polymers obtained by using low initiator concentration ($[I] = 1 \times 10^{-3}$ M) do not exhibit the characteristic absorption band of the thioxanthone moiety.

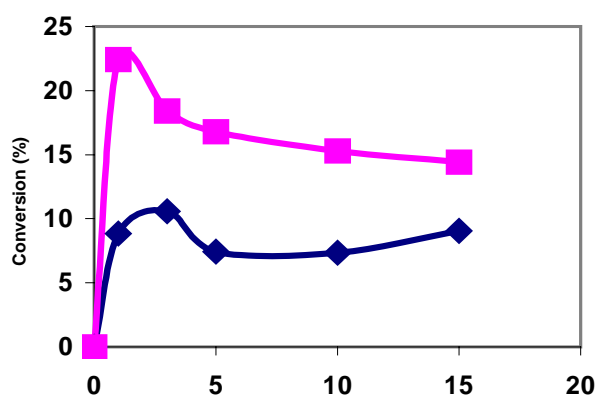


Figure 5. Photopolymerization of methyl methacrylate [4.68 mol.l^{-1}] by using TX-S-CH₂-COOH in DMF for 10 min (◆) and 15 min (■).

On the contrary, the UV-vis spectra of the corresponding poly(methyl methacrylate) PMMA obtained by using a very high initiator concentration ($[I] = 5 \times 10^{-3}$ M) and purification by several precipitation presents an absorption band with a shoulder at 383 nm which is similar to the absorption spectrum of pure TX-S-CH₂-COOH.

The covalently attached TX-moiety to the polymer is more clearly shown by luminescence spectroscopy. Figure 6 shows fluorescence and phosphorescence spectra of the same solutions of the UV-vis measurements (As can be seen from Figure 6, fluorescence and phosphorescence spectra in 2-methyltetrahydrofuran at 296 and 77 K, respectively, of the initiator and the corresponding polymer are very similar.

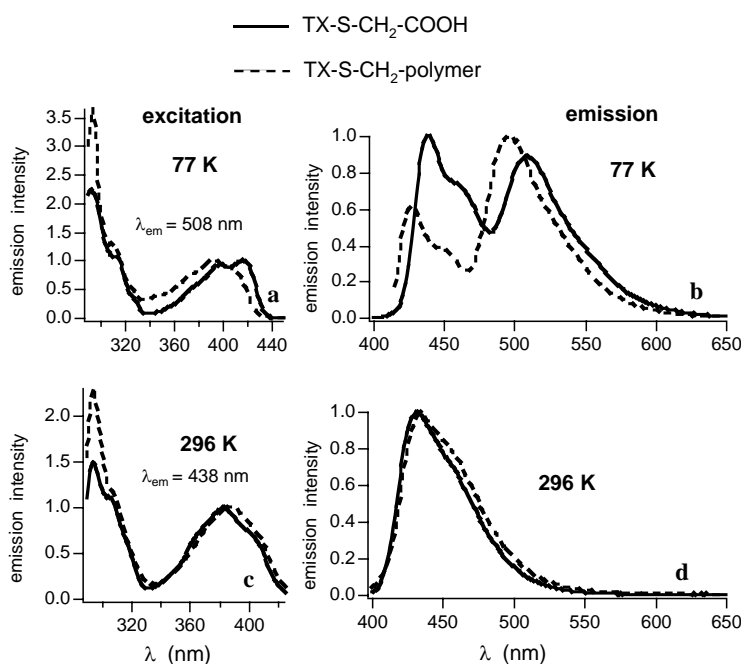


Figure 6. Dashed lines: luminescence excitation (left) and emission spectra (right) of 2-methyltetrahydrofuran solutions at room temperature (c,d) or frozen matrixes at 77 K (a,b) of the purified polymer (several precipitations) obtained by photopolymerization of methyl methacrylate initiated by TX-S-CH₂-COOH (5×10^{-3} M). For comparison, the luminescence spectra of pure TX-S-CH₂-COOH are also shown (solid lines).

Methyltetrahydrofuran solutions at room temperature (c, d) or frozen matrixes at 77 K (a, b) of the purified polymer (several precipitations) are obtained by photopolymerization of methyl methacrylate initiated by TX-S-CH₂-COOH (5×10^{-3} M). For comparison, the luminescence spectra of pure TX-S-CH₂-COOH are also shown (solid lines).

The slight blue shift may be attributed to the slightly different structure of the polymer linked TX compared to the pure initiator. The excitation spectra for the emission signals (Figure 6, dashed lines) are in good agreement with the absorption spectrum of the precursor TX-S-CH₂-COOH (solid lines). In addition, the phosphorescence lifetimes at 77 K are also very similar; 127 and 123 ms, respectively.

Based on the study on the above spectroscopic and flash photolysis of TX-S-CH₂-COOH, and polymerization studies, we proposed Scheme 4 illustrating the major processes that may occur during photoinitiated polymerization.

Under low initiator concentrations, the dominant path of the reaction is intramolecular electron transfer followed by hydrogen abstraction and decarboxylation. At the concentrations above 5×10^{-3} M, however, the respective intermolecular reactions may be operative.

It should also be noted that there has been several reports on the use of one-component polymeric *Type II* photoinitiators (Table 2). Polymeric photoinitiators

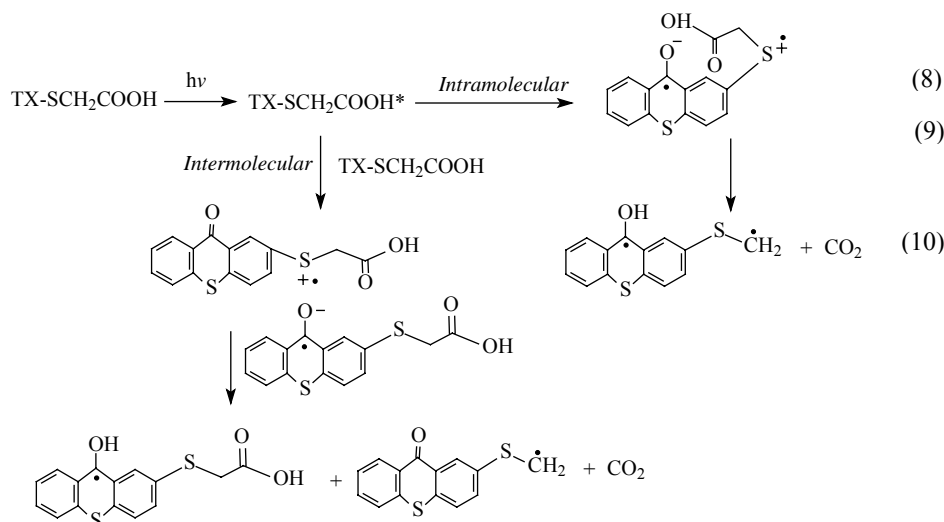

Scheme 4. Photoinitiated free radical polymerization by TX-S-CH₂-COOH.

Table 2. One-component Polymeric *Type II* Photoinitiators.

Structure	Synthesis
	Step polymerization
	Step polymerization
	Step polymerization
	Addition reaction between TX-epoxide and poly(ethyleneimine)
	Addition reaction between TX-epoxide and amino dendrimer

overcome the problems in curing applications associated with low odor and toxicity, and good storage stability. Yin and co-workers^{25, 26} synthesized three kinds of polymeric photoinitiators containing in-chain thioxanthone and amines in the structure by step-polymerization. It was found that the efficiency of the photopolymerization was mainly affected by the structure of amine in the polymeric photoinitiator. They have also prepared²⁷ polymeric amine bearing side-chain thioxanthone photoinitiators by addition of epoxy thioxanthone (TX-epoxide) to poly(ethyleneimine). In another study²⁸, the same group has developed dendritic polymeric photoinitiators containing thioxanthone and in-chain amines and they found that the dendritic photoinitiator initiates the polymerization much more efficiently than the low-molecular weight model compound.

Conclusion

In conclusion, it is clear that one-component thioxanthone based photoinitiators are very attractive, since they do not require an additional hydrogen donor and initiate the polymerization of both acrylate and styrene monomers in the presence and absence of air. In addition, because of the thioxanthone structure they possess excellent optical absorption properties in the near UV spectral region, ensuring efficient light absorption from most UV-curing tools. These properties suggest that they may find use in a variety of practical applications.

References

1. Pappas, S. P., 1978, *UV Curing Science and Technology*; Technology Marketing Corp.: Norwalk, CT.
2. Fouassier, J. P., 1995, *Photoinitiation, Photopolymerization and Photocuring*; Hanser Verlag: Munich.
3. Dietliker, K., 1991, *Chemistry & Technology of UV & EB Formulation for Coatings, Inks & Paints*. SITA Technology Ltd.: London, Volume III.
4. Davidson, R. S., 1999, *Exploring the Science, Technology and Applications of UV and EB Curing*, SITA Technology Ltd.: London.
5. Mishra M. K.; Yagci, Y., 1998, *Handbook of Radical Vinyl Polymerization*, Marcel Dekker Inc.: New York, Chapter 7
6. Davis M. J.; Doherty J.; Godfrey, P. N.; Gren, P. N.; Yung, J. R. A.; Parrish, M. A. J., 1978, *Oil. Col. Chem. Assoc.*, 11, 256
7. W. Schnabel., 1986, *J. Radiat. Curing*, 13, 26
8. G. Amirzadeh, W. Schnabel., 1981, *Makromol. Chem.*, 182, 2821.
9. N.S. Allen, F. Catalina, P.N. Green, W.A. Green, 1986, *Eur. Polym. J.*, 22, 793.
10. S. Yates, G.B. Schuster, 1984, *J. Org. Chem.*, 49, 3349.
11. K. Meier, H. Zweifel, 1986, *J. Photochem.*, 35, 353.
12. P.N. Green, 1985, *Polym. Paint. Resins*, 175, 246.
13. M.J. Davis, G. Gawne, P.N. Green, W.A. Green, 1986, *Polym. Paint. Colour J.*, 176, 536 .
14. Hammond, G. S.; Wamser, C. C.; Chang, C. T.; Baylor, C.J., 1970, *J. Am. Chem. Soc.*, 92, 6362.
15. G. Berner, G. Rist, W. Rutsch, R. Kirchmayr, 1985, *Radcure Basel*, Technical Paper FC85-446, SME Ed., Dearborn, MI
16. Turro, N. J., 1991, *Modern Molecular Photochemistry*; University Science Books, Sausalito, CA.
17. G. Li Bassi, L. Cadona, F. Broggi, 1986, *Radcure 86*, Technical Paper 4-27, SME Ed., Dearborn, MI.
18. L. Çokbağlan, N. Arsu, Y. Yagci, S. Jockusch, N. J. Turro, 2003, *Macromolecules.*, 36(8), 2649.

19. R. S. Davidson, K. Harrison and P. R. Steiner, 1971, *J.Chem.Soc.(C)*, 3480.
20. R. S. Davidson, and P. R. Steiner, 1972, *J.Chem.Soc.Perkin II*, 1358.
21. Davidson, R. S.; Steiner, P. R., 1971, *J.Chem.Soc., Chem. Commun.*, 1682.
22. Barthomolew, D. R.; Brimage, D. R. G.; Davidson, R. S., 1971, *J.Chem.Soc., Chem. Commun.*, 3482.
23. Carmichael, I.; Hug, G. L., 1989, In *CRC Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, Vol. 1, pp. 369-403.
24. Dalton, J. C.; Montgomery, F. C., 1974, *J. Am. Chem. Soc.*, 96, 6230.
25. X. Jiang, J. Yin, 2004, *Macromol. Rapid Commun.*, 25, 748 .
26. X. Jiang, H. Xu, J. Yin, 2004, *Polymer*, 45, 133.
27. X. Jiang, J. Yin, 2004, *Polymer*, 45, 5057.
28. X. Jiang, J. Yin, 2004, *Macromolecules*, 37, 7850.